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Preparation of Perovskite-type Oxides with Large Surface Area by Citrate Process

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Well-crystallized perovskite-type oxides could be synthesized at temperatures as low as 550-650 °C by the calcination of amorphous citrate complex precursors. The large specific surface areas of the oxides obtained suggest that the citrate process is very promising for preparing perovskite-type oxide catalysts for practical use.

Perovskite-type oxides containing transition metals, especially Co and Mn, have been known to show high catalytic activity for the complete oxidation of hydrocarbons and their potentiality of replacing noble metals as combustion catalysts has been examined extensively. Since Ohbayashi et al.[1] reported that the preparation of perovskite-type oxides from metal acetates had an advantage over those from metal oxides, carbonates or oxalates in moderating the preparation conditions, the acetate process has been widely used in catalyst researches. However, the catalyst thus prepared has a rather small specific surface area less than 10 m^2/g, so that new preparation methods which give a catalyst with a sufficiently large specific surface area and/or a supported catalyst with finely dispersed particles of perovskite-type oxides are eagerly awaited for practical purposes. Recently Sale et al.[2,3] adopted a citrate process for preparing several perovskite oxides. Their aim was to obtain highly homogeneous and pure compounds at high process yields, applying mostly high calcination temperatures above 1000 °C. In this paper, we report that by the citrate process alkali earth metal doped as well as undoped perovskite-type oxides can be prepared at relatively low calcination temperatures and thus the process is very promising for preparing perovskite-type oxides with large surface area.

Amorphous citrate precursors were synthesized essentially according to Sale et al.[2,3] Nitrates of constituent metals of a perovskite-type oxide to be prepared were dissolved in water at the desired proportion and mixed with an aqueous solution of citric acid. The molar ratio of citric acid to total metal cations, R, was found to be important and fixed at unity in this study. Water was evaporated from the mixed solution using a rotary evaporator at 60-70 °C until a sol was obtained. The sol was further dehydrated at 60-70 °C for 5 h in a vacuum oven to yield a solid amorphous citrate precursor. The thermal decomposition behavior of the precursor was examined by means of thermogravimetry (TG) in air at a heating rate of 10 °C/min. The products calcined at various temperature between 200 °C and 800 °C were characterized by X-ray diffraction (XRD) and infrared
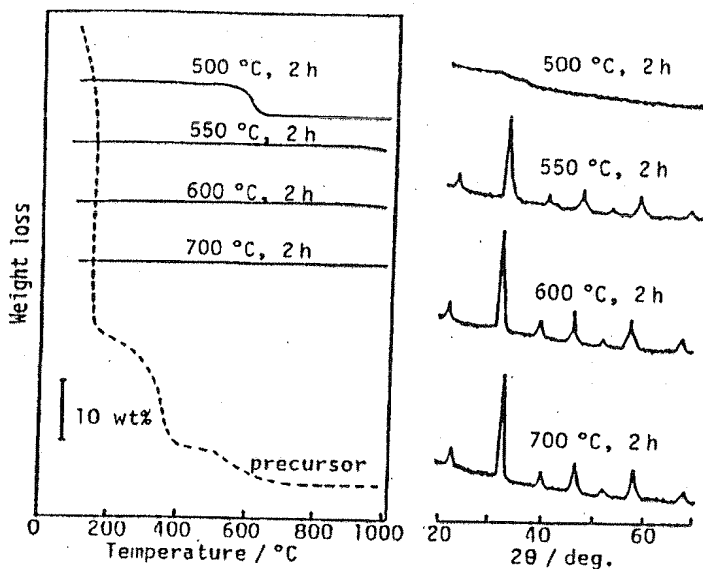
Fig. 1. TG curves of a precursor for La-
       $Co_{0.4}Fe_{0.6}O_3$ and its calcination
       products (left) and XRD patterns of
       the corresponding products (right).

Fig. 2. Infrared spectra of a pre-
       cursor for $LaCo_{0.4}Fe_{0.6}O_3$
       and its calcination prod-
       uct.

spectroscopy (IR). Surface area was mea-
sured by BET method at liquid nitrogen tem-
perature (N_2 adsorption).

    Amorphous citrate precursors were found
to undergo thermal decomposition stepwise
before perovskite-type oxides were obtained.
As an example, Fig. 1 shows the TG curves of
a precursor for $LaCo_{0.4}Fe_{0.6}O_3$ and the products obtained by calcining the precur-
sor at 500-700 °C for 2 h as well as the XRD patterns of the calcination pro-
ducts. The precursor is seen to decompose in three steps: 100-150 °C (first),
300-400 °C (second) and 500-700 °C (third). This behavior was essentially the
same for all the precursors prepared in this study except for minor variations in
temperature ranges for the respective steps. When the precursor of $LaCo_{0.4}Fe_{0.6}O_3$
was calcined at 500 °C for 2 h, TG analysis showed a weight loss at 550 °C as
shown in Fig. 1 which corresponded to the third-step decomposition of the precur-
sor. The products calcined above 550 °C no longer showed weight loss. In agree-
ment with this, the XRD patterns showed that the former product was almost amor-
phous while the latter ones were well crystallized $LaCo_{0.4}Fe_{0.6}O_3$ of a single
phase. It follows that crystallization is induced at the third-step decomposi-
tion.

    The IR spectra of the same precursor and its calcination products are de-
picted in Fig. 2. The precursor and the product calcined at 200 °C gave somewhat
complicated spectra. Two strong bands at ca. 1580 and ca. 1410 cm^{-1}, common to
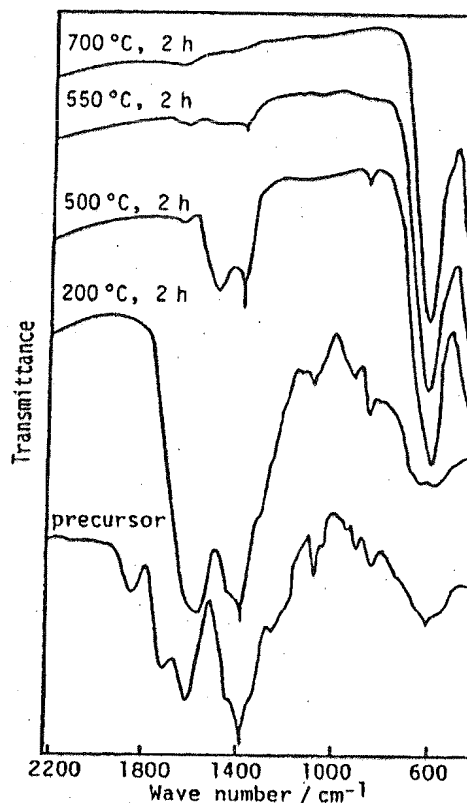both samples, were well assigned to the asymmetric and symmetric C-O stretching

vibrations of ionized carboxylate, respectively, though the latter band was superposed by a sharp 1385 cm^{-1} band responsible to ionic nitrate. This means that the hydrogen atoms of carboxyl groups of citric acid were replaced by metal cations to form a citrate complex. Bands at 1710 and 1840 cm^{-1}, assignable to the C=O stretching mode of free citric acid or its anhydride, were observed in the precursor sample but completely disappeared in the calcination product at 200 °C, showing that the free citric acid components were eliminated at the first-step decomposition. Calcination at 500 °C or above resulted in simpler IR spectra. Strong bands at ca. 595 and 400 cm^{-1}, assignable to M-O stretching and O-M-O deformation modes of $LaMO_3$ (M: Cr, Mn, Fe, Co), respectively,[4,5] were almost unchanged with increasing calcination temperature. On the other hand, two pairs of bands, (1480 and 1400 cm^{-1}) and (1385 and 850 cm^{-1}), assigned to monodentate carbonate and ionic nitrate, respectively, were distinct after calcination at 500 °C, very weak at 550 °C and invisible at 700 °C. From these IR spectra, it was concluded that the second- and the third-step decompositions corresponded, respectively, to the break-up of the citrate complex and to the elimination of residual CO_3^{2-} and NO_3^{-}. It was noted that the IR spectrum after calcination at 500 °C revealed the formation of a framework of perovskite structure while XRD indicated an amorphous state.

To prepare various perovskite-type oxides by the citrate process, corresponding precursors were synthesized and calcined at various temperature. Table 1 summarizes the calcination products obtained in each case as determined by XRD. The oxides in which A sites were fully occupied by La ions (group I) were obtained as well-crystallized single-phase compounds in the temperature range of 550-650 °C. The minimum temperature for perovskite-phase formation was found to almost coincide with that of the third-step decomposition. The oxides in which A sites were partially substituted by Ca ions (group II) could also be synthesized at 550 °C as single-phase compounds up to high Ca contents (0.6 for Co and 0.8 for Mn). On the other hand, the Sr containing systems (group III) were found to be more difficult to prepare. When Sr content was small like $La_{0.8}$-

Table 1. Phases produced by calcining amorphous citrate precursors (XRD)

	Sample	Calcination temperature / °C				
		200	550	600	650	800
I	$LaMnO_3$	Am	Am	Am	P	P
	$LaFeO_3$	Am	P	P	P	P
	$LaMn_{0.8}Cu_{0.2}O_3$	Am	Am	P	P	P
	$LaMn_{0.6}Cu_{0.4}O_3$	Am	Am	P	P	P
	$LaCo_{0.4}Fe_{0.6}O_3$	Am	P	P	P	P
	$LaCo_{0.8}Cu_{0.2}O_3$	Am	P	P	P	P
	$LaCoO_3$	La_2CoO_4		P	P	P
II	$La_{1-x}Ca_xCoO_3$ (0.2≤x≤0.6)	Am	P	P	P	P
	$La_{1-x}Ca_xMnO_3$ (0.2≤x≤0.8)	Am	P	P	P	
III	$La_{0.8}Sr_{0.2}MnO_3$	Am	Am	P	P	P
	$La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$	Am	P	P	P	P
	$La_{0.6}Sr_{0.4}MnO_3$	$Sr(NO_3)_2$		$P + SrCO_3 + BO_n$		
	$La_{0.8}Sr_{0.2}CoO_3$	$Sr(NO_3)_2$		$P + SrCO_3 + BO_n$		
	$La_{0.8}Sr_{0.2}Co_{0.4}Fe_{0.6}O_3$	$Sr(NO_3)_2$		$P + SrCO_3 + BO_n$		
	$La_{0.6}Sr_{0.4}Co_{0.8}Cu_{0.2}O_3$	$Sr(NO_3)_2$		$P + SrCO_3 + BO_n$		

Am ; amorphous, P ; perovskite-type oxides, BO_n ; oxide of B cation

$Sr_{0.2}MnO_3$ and $La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$, single-phase perovskite-type oxides were synthesized. At high Sr contents, however, products were mostly a mixture containing perovskite-type oxides. In such unfavorable cases, strontium nitrate was detected after calcination at 200 °C. The nitrate was then converted to strontium carbonate above 550 °C and a single-phase oxide was obtained only after calcination at temperatures above 800 °C. The separation of strontium nitrate from the precursor was also reported by Sale et al.[2,3]

Table 2. Specific surface areas of perovskite-type oxides prepared by citrate process and acetate process

Sample	Citrate process		Acetate process	
	Calc. temp	Surf. area	Calc. temp	Surf. area
	°C	$m^2 \cdot g^{-1}$	°C	$m^2 \cdot g^{-1}$
$LaFeO_3$	550	14.4	850	4.4
$LaMnO_3$	650	44.8	850	7.3
$LaCoO_3$	600	11.3	850	2.2
$LaCo_{0.4}Fe_{0.6}O_3$	550	22.7	850	3.3
$LaMn_{0.8}Cu_{0.2}O_3$	600	32.1	850	7.3
$LaMn_{0.6}Cu_{0.4}O_3$	600	33.0	850	7.5
$La_{0.8}Sr_{0.2}MnO_3$	600	36.4	850	8.2
$LaCo_{0.8}Cu_{0.2}O_3$	550	24.7	——	——
$La_{0.8}Ca_{0.2}MnO_3$	650	27.3	——	——
$La_{0.2}Ca_{0.8}MnO_3$	650	29.9	——	——
$La_{0.4}Ca_{0.6}CoO_3$	600	14.3	——	——

In Table 2, the specific surface areas of selected perovskite-type oxides prepared by the citrate process are listed, some of them being compared with the corresponding data for the conventional acetate process. The lowest temperature for single-phase perovskite formation was 850 °C in the acetate process. It is clear that the citrate process can adopt calcination temperature which is 200-300 °C lower than in the acetate process. This lowering of calcination temperature appears to result in the formation of oxides with specific surface areas 3 to 7 times larger than those prepared by the acetate process. It was found with $La_{0.8}Sr_{0.2}MnO_3$ that, even when the citrate process was applied, the specific surface area decreased with an increase in calcination temperature and became almost equal to that of the oxide prepared by the acetate process when calcination temperature was the same (850 °C). This again confirms that the advantage of the citrate process is associated with the lowering of calcination temperature. It seems that the formation of a citrate complex in the precursor state effectively keeps the constituent metal cations dispersed homogeneouly and thus makes easier the formation of perovskite-type oxides.

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